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ORGANIC PHOSPHORUS COMPOUNDS FOR INSECT PESTS CONTROL

This report giving data on phosphorus compounds is an excerpt from a long article by Dr H. Fuerst (Magdeburg), "Progress in Pest Control Chemistry," The remainder of the article contained generally known data, based largely on material either published or available in the US.

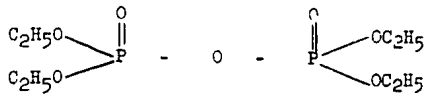
The Plant Protection Laboratory of the Bayer Dye Factories at Elberfeld has been developing new insecticides since 1934. Most of this work was done by G. Schrader.(1) These chemicals have become highly important for special pest-control purposes. Three groups of compounds were investigated, which became important in the following chronological order:

a. Phosphoric Acid Esters of the Bladan type (TEPP and HETP)

b. Thiophosphoric Acid Esters of the E 605 and E 838 type

c. Intratherapeutically active substances of the Pestox III type.

In the history of the development of the above compounds, Schrader describes how he abandoned his original idea of synthesizing organic fluorine compounds to make insecticides, and how he finally found the first powerful insecticide of the phosphorus alkoxy series, the pyrophosphoric acid tetraethyl ester (TEPP):



a. A patent for this substance was taken out in 1938, but it did not become known until 1945, when its discoverer was interrogated by FIAT of the US Army.(2) Soon afterward, its production abroad was started and it was introduced there under the name of TEPP. At the same time, work was done on hexaethyl tetraphosphate (HETP), obtained by the older method from phosphorus oxychloride and triethyl phosphate:

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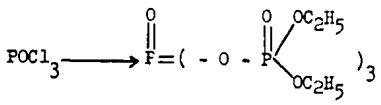
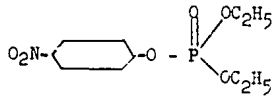


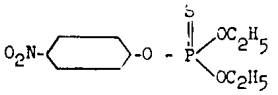
By the more recent method, it is obtained directly from phosphorus oxychloride and alcohol at 140°C. The yield is high; HCl and ethyl chloride are distilled off at reduced pressure.(3) The technical product is not homogeneous. It is called Bladan.(4) It contains an ester mixture of the above general formula. Up to 30 percent of it may be tetraethyl pyrophosphate, which is the effective component. If the substance contains less than 20 percent of this compound, it is known as HETP; if the content is above 40 percent, it is called TEPP.(5)

Bladan became known all over the world as an agent against plant lice and caterpillars, equal to nicotine in effectiveness, and was used in 1:1000 aqueous solution. Due to the hydrolytic ester spliting the solution is unstable. The toxicity of Bladan to warm-blooded animals equals that of nicotine. In Germany, it has now been replaced by new products based on phosphoric acid esters, such as E 605.

b. The new insecticide E 605 first became known abroad subsequent to interrogation of Elberfeld chemists after the war. After thorough research on phosphoric acid esters, they had succeeded in finding compounds which had higher stability to water and alkalies than Bladan. Over the tetraethyl dithiopyrophosphates, which by themselves turned out to be useful, p-nitrophenyl diethyl phosphoric acid ester, called E 600, was obtained. It is also known by the name of Mintacol:



It is too toxic to be used as an insecticide. However, it contracts the pupils of the eyes and is therefore suitable as a pharmaceutical. Apparently, combining of experiences gained with the hydrolysis-resistant dithiophosphoric acid ester and with E 600 led to the production of p-nitrophenyl diethyl thiophosphoric acid ester, called E 605:



Today, E 605 is made by the following method: Phosphorus trichloride is quantitatively converted with sulfur to thiophosphorus trichloride. This is then treated in an alcohol solution with the calculated quantity of sodium ethylate, and the isolated intermediate product (diethoxy thiophosphoric acid) is made to react with p-nitrophenol sodium.(6) After the solvent has been removed, the crude product is obtained directly in the form of a yellow oil which is insoluble in water.

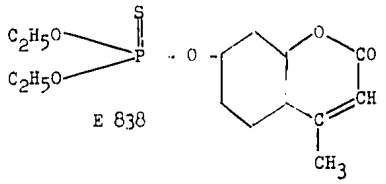
The usual modifications of its constitution, i.e., substitution of other alkyl groups, replacement of the $-No_2$ group, etc., did not improve the effectiveness of the substance.

Foreign publications (7) also describe E 605 as the dimethyl thiophosphate of p-nitrophenol, while parathione is supposed to be diethyl thiophosphate.

E 605 resists hydrolysis and is thus sufficiently stable in aqueous spray solutions. It is a contact, food, and respiration poison for pests. Its main use as an insecticide is in the control of pests in orchards and gardens, for which nicotine, pyrethrum, and lead arsenate were principally used before. It is supplied in different forms: as "E 605 forte" with 74 percent effective substance and 26 percent emulsifier (8); as "Folidol," an approximately 10 percent oil concentrate; and as "E 605 dust." All these are toxic for warm-blooded animals. A series with decreasing toxicity can be arranged as follows: Bladan, E 605, Dieldrin, nicotine, Aldrin, Chlordane, DDT, gamma-HCH [gamma-hexachlorocyclohexane], pyrethrum.

A preparation similar to E 605 is manufactured in Western Germany under the name "Pox" (T 47), made by Borchers Bros. of Goslar, and under the name of "Wofatox" in the German Democratic Republic.(9) Abroad it is known as "Parathione" or "Thiophos."

E 605 is not sufficiently effective against the potato bug. Only after the war, in 1947, was a selective insecticide, E 838, developed to control this pest. This substance, also known as "Potasan," is the result of further systematic work on the E 605 series. It is the thiophosphoric acid ester of 4-methyl-7-hydroxycoumarin. It was used on a large scale in 1950, is both a food and a contact poison, according to the manufacturer's statements, and will also kill the eggs of the bug. It is hard to tell just what prompted the people who developed this product to use the complex phenol 4-methyl-7-hydroxycoumarin. On the other hand, Butenandt (10) in his work on the constitution of rotenone states that one of its essential components is a coumarin nucleus. He also mentions that two other substances of more simple structure, bergaptene and xanthotoxin, which are coumarone-coumarins, resemble rotenone insecticide in their formula and physiological properties.



E 838

C. The British systemic insecticide of the intratherapeutic type, Pestox III (octamethylpyrophosphoric acid tetra-amide), while less poisonous than E 605 or Bladan, is still strongly toxic to warm-blooded animals.

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4. Wolfen Dye Plant

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6. cf. 3

7. cf. 3

8. cf. 3

9. cf. 4

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